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Enhanced COD (Chemical Oxygen Demand) Removal from Pharmaceutical Wastewater Using Powdered Activated Carbon Addition to an Activated Sludge System

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ENHANCED COD REMOVAL FROM PHARMACEUTICAL WASTEWATER USING POWDERED ACTIVATED CARBON ADDITION TO AN ACTIVATED SLUDGE SYSTEM

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16. ABSTRACT

Wastewater generated by the pharmaceutical manufacturing point source Sub-categories A (Fermentation Products) and C (Chemical Synthesis Products) are characterized by high COD concentrations (10,000 mg/l and higher). Plants in these subcategories typically employ secondary treatment to meet best practicable control technology currently available (BPT). However, COD levels in the effluent discharge usually remain quite high.

The objective of this project was to demonstrate, through a continuous pilot plant study, the capability of powdered activated carbon technology to achieve additional COD reductions from pharmaceutical plant wastewater which has been treated biologically. Powdered activated carbon dosages of 208, 496, 327 and 1,520 mg/l were investigated.

The results of the study determined that powdered activated carbon had a significant effect on effluent COD concentrations. This paper will discuss these results as well as other important findings from this industrial wastewater research project.

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ENHANCED COD REMOVAL FROM PHARMACEUTICAL WASTEWATER USING POWDERED ACTIVATED CARBON ADDITION TO AN ACTIVATED SLUDGE SYSTEM

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INTRODUCTION

The pharmaceutical manufacturing point source category manufactures biological products, medicinal chemicals, botanical products and pharmaceutical products covered by Standard Industrial Classification Code Numbers 2831, 2833 and 2834, as well as other commodities. The industry is characterized by diversity of product, process, plant size, as well as wastewater quantity and quality. For example, many plants will generate wastewaters with chemical oxygen demand (COD) concentrations ranging from 500 to 1500 mg/l whereas wastewaters from Subcategories A (Fermentation Products) and C (Chemical Synthesis Products) may have COD concentrations up to 10,000 mg/l and higher (1). These latter plants may be able to discharge treated wastewaters meeting Best Practicable Control Technology Currently Available (BPT), which is defined as a COD removal of 74 percent (1). However, these treated wastewaters may still contain COD concentrations of 2,600 mg/l and higher.

On November 26, 1982, the U.S. Environmental Protection Agency (EPA) proposed Best Available Technology Economically Achievable (BAT) and New Source Performance Standards (NSPS) designed to control the discharge of the nonconventional pollutant, COD, as well as other pollutants from pharmaceutical manufacturing facilities (2,3). The industry commented that the proposed regulations could not be met by A and C subcategory plants based on the proposed technology.

On October 27, 1983, the EPA promulgated final Pharmaceutical Manufacturing Point Source Category Effluent Limitations Guidelines, Pretreatment Standards and New Source Performance Standards (4,5). In this rulemaking, the Agency decided to return to the 1976 BPT subcategorization scheme and, as a result, the 1982 proposed COD regulations are no longer a valid point of comparison. A final decision on appropriate BAT limitations and NSPS for COD was postponed until additional information could be obtained on applicable COD removal technologies and their achievable concentrations.

By way of responding to these additional information needs, the EPA initiated a program which included studies designed to evaluate the ability of activated carbon adsorption technologies to reduce the effluent COD concentrations.

Two technologies were evaluated at a Subcategories A and C pharmaceutical manufacturing plant which employed secondary treatment and reported high COD concentrations in their discharge monitoring report. The two technologies were:

1. Powdered activated carbon (PAC) addition to the activated-sludge aeration basin.
2. Granular activated carbon (GAC) treatment of the secondary effluent.

This paper presents the results of the PAC/activated sludge studies. From September to December, 1984, an eighty-three (83) day study was conducted using the biological pilot plant shown on Figure 1 as the control and the two biological systems illustrated on Figure 2 as the experimental (PAC fed) systems. The three activated sludge units were operated in parallel. The objective of this study was to evaluate the effectiveness of powdered activated carbon addition to the activated sludge process to reduce effluent COD concentrations.

SYSTEM OPERATION

Raw pharmaceutical wastewater collected just before entering the full-scale plant aeration basins was used as the feed to the pilot plants. This flow consisted of neutralized and equalized pharmaceutical waste combined with a nominal amount of macerated, chlorinated sanitary waste.

The two experimental activated sludge systems shown on Figure 2 were identified as Biological Treatment Systems No. 1 and No. 2 (BTS-1 and BTS-2). Each system consisted of an aeration tank (5940 liters in BTS-1 and 5560 liters in BTS-2) and a 2840 liter circular center feed clarifier. Each aeration tank had three aeration cells in series and the air flow to each cell was controlled independently. Pumps were used to supply wastewater, return sludge and add chemicals for each system. Powdered activated carbon slurry was pumped to the experimental systems and sodium hydroxide was pumped to all three systems on an as needed basis to maintain an adequate pH range.

The control pilot plant (BTS-3) consisted of an aeration tank with three aeration cells in series (total volume of 180 liters) and a 47 liter secondary clarifier. (Detailed description of this system is provided in

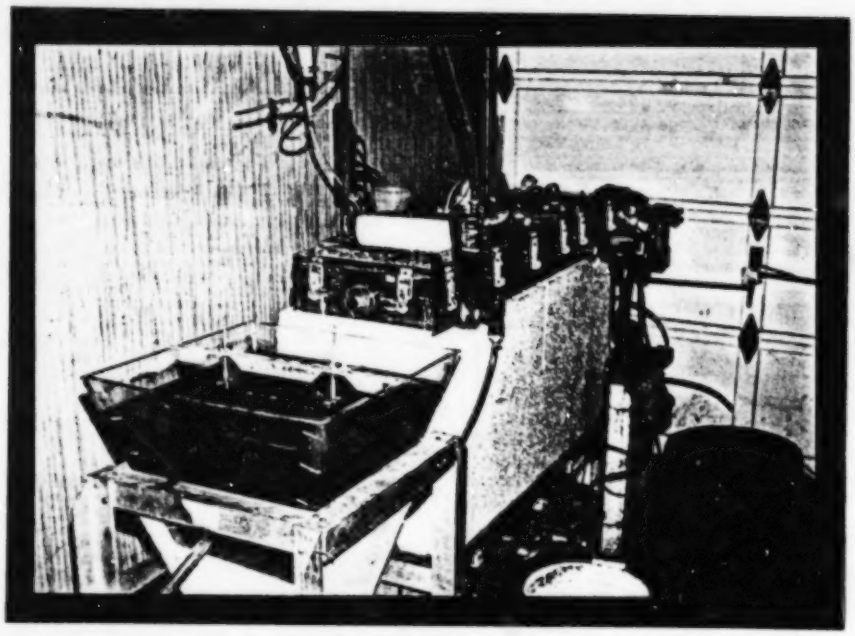

Figure 1. Control Biological Pilot Plant

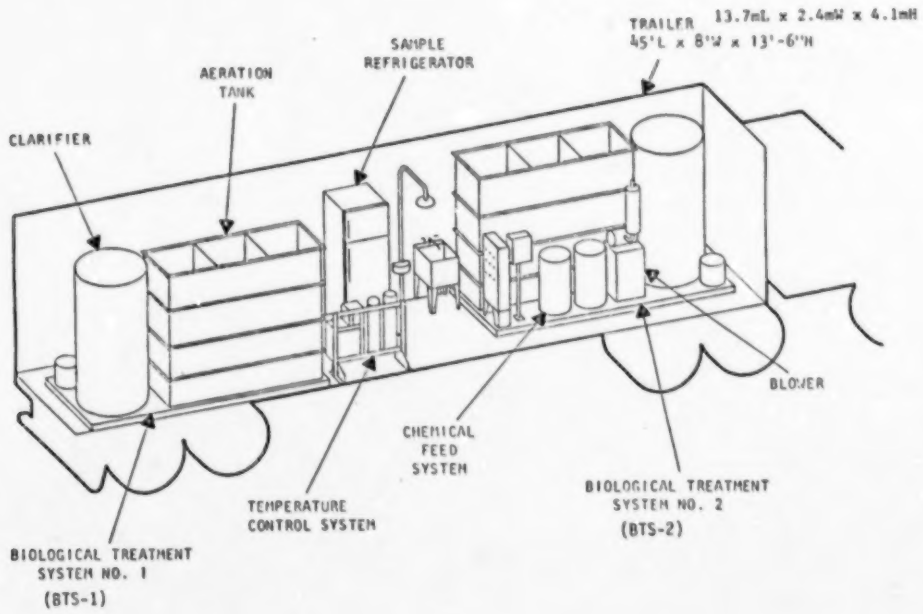

Figure 2. PAC Fed Biological Pilot Plants

reference 6.) Peristaltic pumps were used to feed wastewater to the system, to recirculate settled sludge and to waste sludge. A schematic diagram of the biological treatment systems is shown on Figure 3. The raw wastewater was pumped to a mixed equalization tank which served as the feed reservoir for each of the three pilot plants.

The targeted aeration basin hydraulic detention times (HRTs) and solids retention times (SRTs) were 3 days and 10 days, respectively, for all systems. The HRT was determined by dividing the aeration volume by the influent flow rate and the SRT was determined by dividing the mass of mixed liquor suspended solids (MLSS) in the aeration basin by the sum of the SS in the effluent and the wasted MLSS. These values were similar to the values used in the full-scale plant prior to the start of the pilot plant tests. Note that solids were wasted from the third cell of each aeration basin so as to allow a more positive control of the SRTs. During the first test period 208 mg/l and 827 mg/l of PAC were added to the influents of BTS-1 and BTS-2, respectively, and in the second test period 496 mg/l and 1520 mg/l of PAC were added to BTS-1 and BTS-2, respectively.

Composite samples were taken of the raw feed wastewater and three clarifier effluents using automatic sampling equipment. Sampling occurred once every half hour, and the sample containers were iced during the collection period. Composite samples of wasted mixed liquor were obtained from the waste solids holding tanks (see Figure 3) immediately before the daily volume of solids was measured and discarded. The contents of each tank were vigorously stirred while taking the sample. Grab samples of PAC slurry to BTS-1 and BTS-2 were collected from the feed line just prior to entering cell #1, placed directly into an analytical dish, dried and weighed.

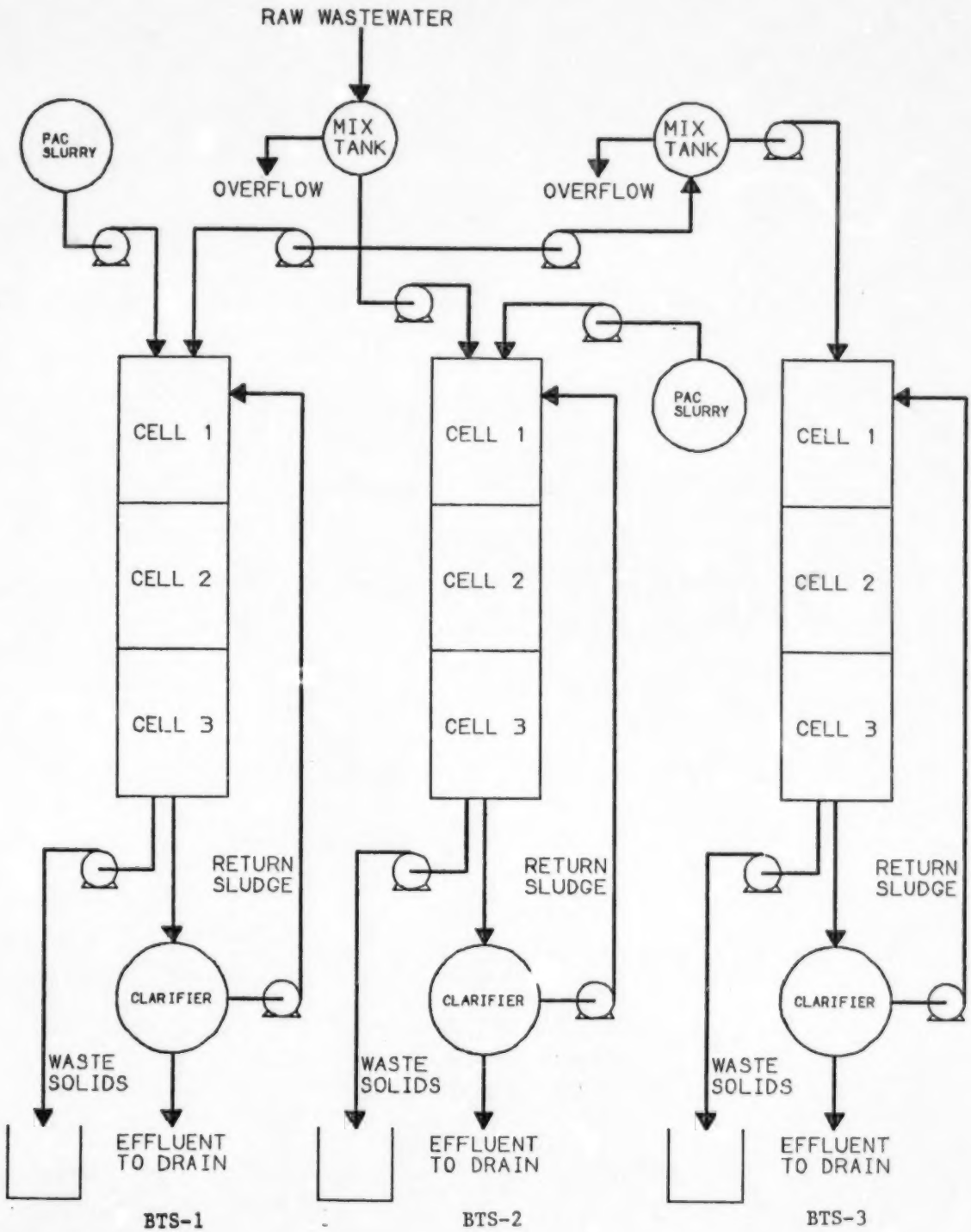

Figure 3. Schematic of Biological Treatment System.

Temperature and dissolved oxygen levels in the aeration basins were performed in-situ, and pH measurements were performed on grab samples of the mixed liquors and the clarifier effluents immediately after sampling. Biochemical oxygen demand (BOD), carbonaceous biochemical oxygen demand (CBOD), COD, suspended solids (SS), volatile suspended solids (VSS) and total solids analyses were performed on-site. Additional samples for analyses such as total organic carbon (TOC), chloride, and nutrients (nitrogen and phosphate, N&P) were shipped to an off-site laboratory. All analyses were performed according to approved EPA methods with the soluble organics performed on the filtrate from 0.45μ filtration.

TEST PHASES

The planned pilot plant operation was scheduled for a series of five phases as described below:

Phase 1 - Start-up

The three biological pilot plants were operated for 10 days after being seeded with mixed liquor from the full-scale aeration basins. The objective of this phase was to determine if the effluents were comparable between each of the three pilot plants.

Phase 2 - Acclimation

Following Phase 1, PAC addition to the influents was initiated for BTS-1 and BTS-2 at rates of 208 mg/l and 827 mg/l, respectively. Single doses of PAC (as 10 percent slurry) were added to each aeration cell of BTS-1 and BTS-2 each day for the first 10 days to reach the calculated equilibrium PAC concentration, and the operation of all three units was continued for an additional 13 days.

Phase 3 - Intensive Test Period

Pilot plant operation continued for 14 days with Phase 2 operational conditions but the frequency of sampling and analysis was increased.

Phase 4 - Transition and Acclimation

PAC feed to the influent of BTS-1 and BTS-2 was increased to 496 mg/l and 1520 mg/l, respectively. Single doses of PAC (as a 10 percent slurry) were again added to each aeration cell of BTS-1 and BTS-2 for each of the first 10 days to reach the calculated equilibrium PAC concentrations. Operation was planned to continue until steady state conditions were achieved based on effluent soluble COD (SCOD) measurements. Following equilibrium attainment a second two-week intensive sampling period (Phase 5) was to be conducted, but as discussed below Phase 5 was not initiated.

OPERATIONAL PROBLEMS

During Phase 3 the pH began to decrease significantly in all three systems. Samples collected for nitrogen analyses confirmed that nitrification was occurring in the three systems and the addition of caustic was initiated to maintain the mixed liquor pH near 7. BTS-1 and BTS-2 also showed evidence of significant denitrification in the clarifiers which caused some of the sludge to float. The sludge recycle rates for these systems were increased in an attempt to maintain small sludge inventories in the clarifiers so as to minimize the floating sludge in the experimental clarifiers.

On two occasions the raw wastewater was very acidic for short periods of time due to acid dumps in the processing plant. The first incident occurred towards the end of Phase 3 and the second one occurred on the fifth day of Phase 4. On both occasions, the low pH was detected early by the pilot plant operators and large amounts of sodium hydroxide were added manually to the

pilot aeration basins to bring the pH back to proper levels.

Near the end of Phase 4 a viscous floating layer of mixed liquor suspended solids (MLSS) formed on the surfaces of the clarifiers and the aeration basins of the two PAC fed systems which resulted in significant reductions in the MLSS in suspension in the aeration basins of BTS-1 and BTS-2. This occurred first for BTS-1 and about 10 days later for BTS-2. It did not occur in BTS-3, the control system. As a result of this problem, the Phase 5 intensive test period was cancelled. However, data generated during Phase 4 just prior to the onset of the viscous layers were used to evaluate the effects of the 496 mg/l and 1520 mg/l PAC feed rates to BTS-1 and BTS-2, respectively.

Also, during Phase 4 (prior to the viscous MLSS layer formation) the aeration basin effluent line plugged and the MLSS overflowed the aeration basin of BTS-2 which resulted in a significant loss of both volatile MLSS (MLVSS) and PAC. As a result the data presented later for the 1520 mg/l PAC system were collected when the system was not in equilibrium, at least as far as the MLSS concentrations are concerned.

TEST RESULTS

Feedwater Quality

A summary of the analysis on the pharmaceutical plant raw wastewater (feed to the pilot plants) is presented in Table 1. The pH was quite variable, ranging from 6.5 to 12.0. Suspended solids averaged 639 mg/l for 83 samples. The raw waste COD was also quite variable, ranging from 2260 to 12,000 mg/l, and averaged 7030 mg/l. The average BOD concentration was 2830 mg/l with a range from 1700 to 4400 mg/l. Although not shown in Table 1 both nitrogen and phosphate were present in adequate amounts in the raw wastewater

(BOD:N and BOD:P ratios were less than 20 and 100, respectively).

TABLE 1. RAW WASTEWATER CHARACTERISTICS

Parameter	Average	Range
pH, units		6.5 - 12.0(83)*
Temperature, ^{o}C	28 (32)	23 - 32
Suspended Solids, mg/l	639 (83)	200 - 1320
Volatile Suspended Solids, mg/l	460 (52)	140 - 800
Chloride, mg/l	1260 (35)	339 - 1700
COD, mg/l	7030 (83)	2260- 12,000
BOD, mg/l	2830 (23)	1700- 4400
TOC, mg/l	1930 (40)	1320- 2830

*( ) Indicates number of observations.

Pilot Systems

During Phase 1 the effluent SCOD from BTS-1 and BTS-2 averaged 754 and 770 mg/l, respectively whereas the effluent from BTS-3 averaged 849 mg/l. This was not a result of design differences between the pilot plants but was a result of an initial problem due to a different air supply used for aeration of BTS-3 (colder) than that used for the other two systems. Once this was recognized, heaters were installed in the aeration basin of BTS-3 and used to raise the temperature to that of the other two systems. The average temperatures of 31, 32 and 30^{o}C for BTS-1, BTS-2 and BTS-3, respectively, during Phase 2, demonstrated this problem was corrected.

A summary of the average operating parameters and effluent quality during Phases 3 and 4 is presented in Table 2. Average HRTs ranged from 3.0 to 3.1 days and average SRTs ranged from 9.4 to 10.0 days. During Phase 3 the average aeration basin temperatures were 32°C and during Phase 4 it ranged from 27 to 28°C and from 25 to 27°C for the two interim test periods, respectively. MLSS for the control system (BTS-3) during the three time periods ranged from 4770 to 4790 mg/1. For the experimental systems (BTS-1 & 2), the MLSS concentrations increased from 5850 to 8830 mg/1 as the PAC addition to the influent was increased from 208 to 1520 mg/1.

The addition of PAC resulted in some improvement in the sludge settleability; however, the MLSS settling rate remained at very low levels (from 0.01 to 0.05 cm/min). The effect of the PAC on the average effluent SCOD concentrations is shown in Table 2 and on Figure 4. During Phase 3 PAC feed rates of 208 and 827 mg/1 resulted in effluent SCODs of 459 and 265 mg/1, respectively, as compared to 825 mg/1 for the control. During Phase 4 a PAC feed of 496 mg/1 resulted in an effluent SCOD of 314 mg/1 as compared to 670 mg/1 for the control. A PAC feed of 1520 mg/1 to BTS-2 in Phase 4 produced an effluent with 194 mg/1 of SCOD and the control effluent contained 583 mg/1. As discussed earlier the MLVSS and the PAC in BTS-2 during Phase 4 were not in equilibrium. If they had been the effluent SCOD would probably have been less than the reported 194 mg/1.

Also shown on Figure 4 is the average total COD for each of the units. The suspended COD (total COD less SCOD) is a function of the effluent SS which in turn depends upon the clarifier efficiency. The average effluent SS varied from 44 to 143 mg/1 for the control unit and from 59 to 190 mg/1 for the PAC fed systems. The addition of PAC had no measurable effect on the effluent

TABLE 2. AVERAGE OPERATING PARAMETER AND EFFLUENT QUALITY VALUES

	Phase 3			Phase 4			
	BTS-1 vs BTS-2 vs BTS-3 (Day 34-47)			BTS-1* vs BTS-3 (Day 62-65)		BTS-2* vs BTS-3 (Day 71-76)	
Operational Data							
Feed Flow, l/min	1.34	1.26	0.044	1.38	0.045	1.27	0.044
PAC Flow, l/min	0.018	0.018	0	0.031	0	0.032	0
RS Flow, l/min##	3.01	4.08	0.163	3.80	0.092	6.37	0.094
Waste ML Flow, l/min	0.419	0.384	0.013	0.367	0.013	0.373	0.013
PAC Dosage, mg/l	208	827	0	496	0	1520	0
F/M, g COD/g MLSS/day	ND**	ND	0.64	ND	0.69	ND	0.79
HRT, days	3.1	3.1	3.0	3.0	3.0	3.0	3.0
SRT, days	9.5	10.0	9.4	9.8	9.7	10.0	9.8
Mixed Liquor Data							
Temp, °C	32	32	32	27	28	25	27
pH (Range)	4.1-7.5	4.5-7.7	6.0-8.7	6.0-7.2	6.6-8.1	6.7-7.5	6.1-7.4
D O, mg/l	3.3	3.4	4.3	3.6	5.0	3.4	4.5
SS, mg/l	5850	7690	4790	7000	4770	8830	4780
Effluent Data							
COD, mg/l	585	532	1070	454	770	334	689
SCOD, mg/l	459	265	825	314	670	194	583
TOC, mg/l	158	110	290	115	NA#	59	NA
CBOD, mg/l	16	15	27	NA	NA	12	15
S-CBOD, mg/l	<6	<5	<8	NA	NA	3	4
SS, mg/l	85	190	143	59	44	108	92
VSS, mg/l	60	158	109	50	46	76	76
Removals							
Ave. Feed COD, mg/l	8120	8120	8120	7420	7420	6810	6810
COD Removal, %	92.8	93.4	86.8	93.8	89.6	95.1	89.9

* Data for periods just prior to onset of viscous floating layers of MLSS on surfaces of aeration basins and secondary clarifiers.

**ND - Not Determined. #NA - Not Analyzed. ##RS-Return Sludge.

soluble CBOD (S-CBOD). Although measured infrequently the S-CBOD was generally less than 10 mg/l for the control and for the PAC fed systems.

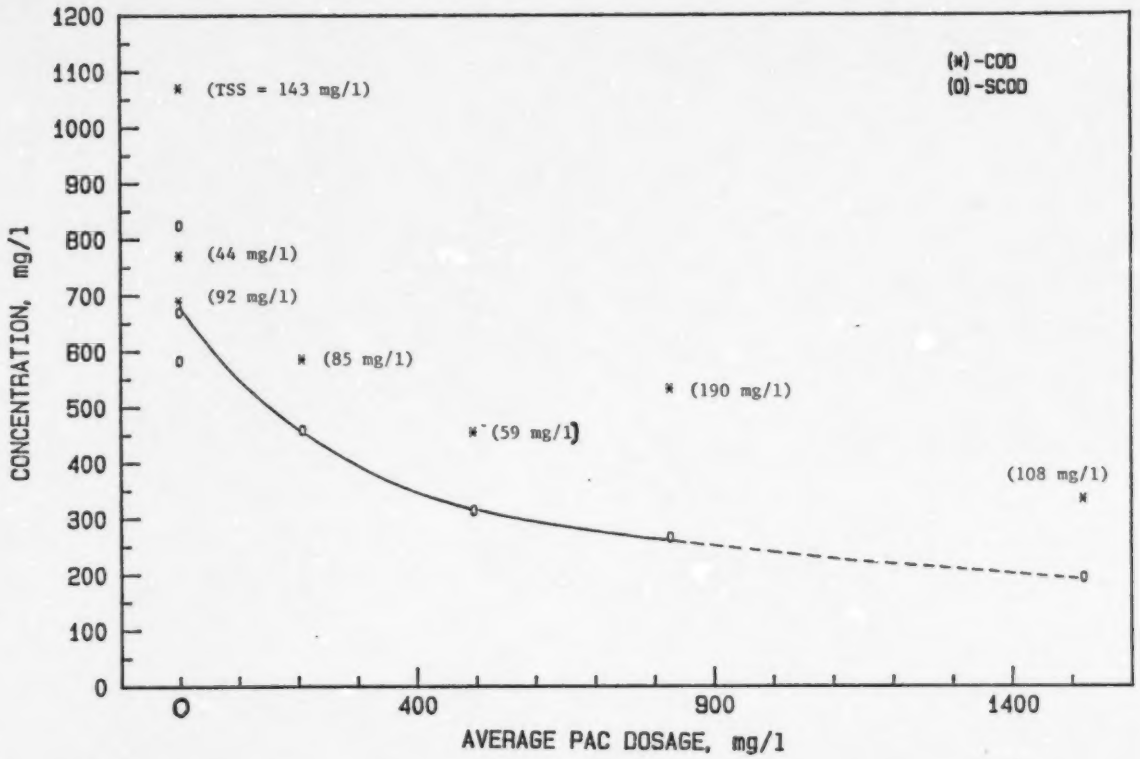

Figure 4. Total and Soluble Effluent COD at Various PAC Dosages.

To further elucidate the effect of PAC addition on SCOD removal the following assumption and calculations were made. It was assumed that the additional SCOD removal by the PAC systems compared to the control operated in parallel was accomplished by the PAC. This allows a calculation of the amount of SCOD removed per unit of carbon added in mg SCOD per mg PAC as shown in Table 3. The SCOD removal/PAC dose (X/M) values were then plotted versus the equilibrium effluent SCOD concentration (C_e) according to the Freundlich equation:

$$\frac{X}{M} = KC_e^{1/n}$$

where: X = amount of SCOD removal attributed to the PAC, mg/l,

M = carbon dose to the influent, mg/l,

C_e = equilibrium effluent SCOD concentration, mg/l,

K,n = empirical constants.

This plot of X/M versus C_e is shown on Figure 5 with the line of best fit having the following equation:

$$\frac{X}{M} = (3.7 \times 10^{-6})\ C_e^{2.1}$$

This equation can be used to provide a reasonable estimate of the PAC requirements to produce any desired effluent SCOD concentration (at least down to C_e = 200 mg/l) for this processing plant's wastewater.

TABLE 3. EVALUATION OF SCOD DATA

Pilot Plant	PAC dose (mg/l)	Effluent SCOD (mg/l)	SCOD Removal by PAC (mg/l)	SCOD Removed / PAC dose (mg/mg)
BTS-1	208	459	366	1.76
BTS-2	827	265	560	0.68
BTS-3	0	825		
BTS-1	496	314	356	0.72
BTS-3	0	670		
BTS-2	1520	194	389	0.26
BTS-3	0	583		

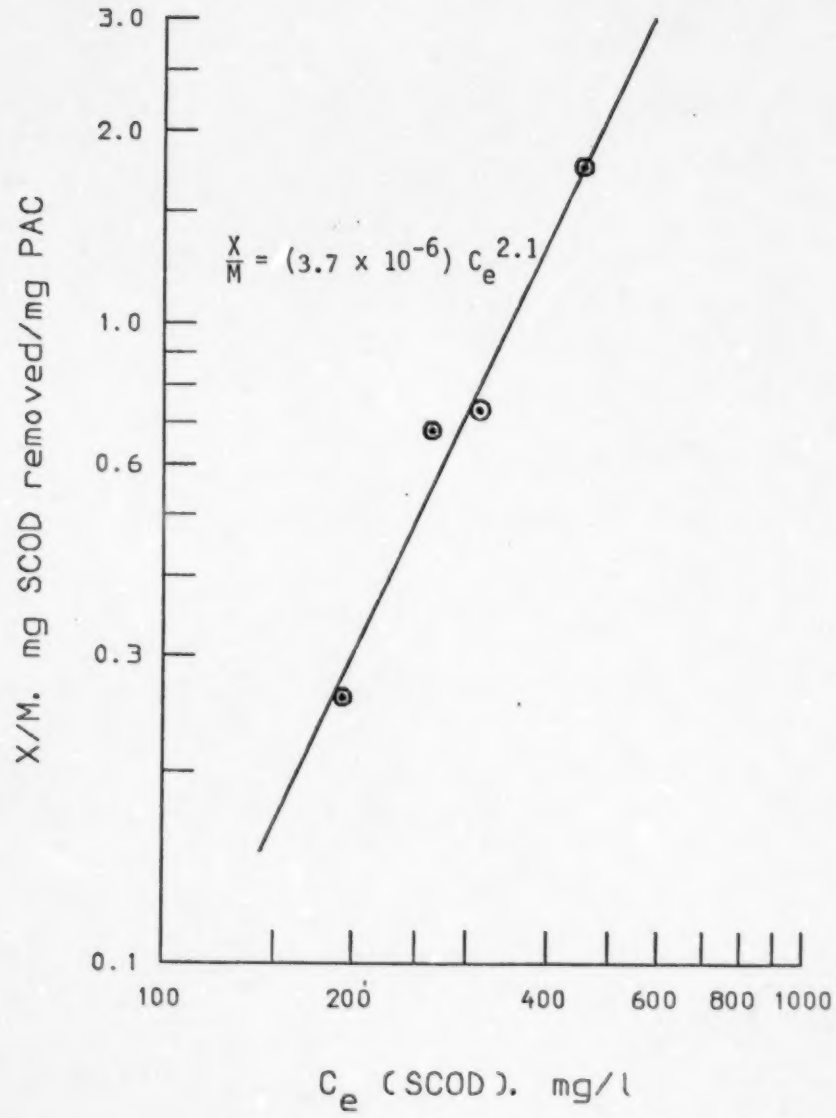

Figure 5. Freundlich Isotherm For SCOD Removal.

CONCLUSIONS

- PAC addition to the activated sludge process can increase the SCOD removal from pharmaceutical manufacturing wastewater.

- The PAC/activated sludge process cannot be recommended as a viable process for this plant's wastewater until the cause of the viscous floating MLSS is identified and adequate safeguards against its occurrence are demonstrated.

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